

Runkel, R.L., McKnight, D.M., and Andrews E.D., 1998, Analysis of transient storage subject to unsteady flow: Diel flow variation in an Antarctic stream: *Journal of North American Benthological Society*, v. 17, no. 2, p 145-154.

Disclaimer: The online document displayed is based on the final draft provided to the editor. Minor discrepancies between the online document and the published version may therefore exist.

Analysis of transient storage subject to unsteady flow: diel flow variation in an Antarctic stream

ROBERT L. RUNKEL

US Geological Survey, Mail Stop 415, Denver Federal Center, Denver, Colorado 80225 USA

DIANE M. MCKNIGHT

Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado 80309 USA

EDMUND D. ANDREWS

US Geological Survey, 3215 Marine St., Boulder Colorado 80303 USA

Abstract. Transport of dissolved material in streams and small rivers may be characterized using tracer-dilution methods and solute transport models. Recent studies have quantified stream/substream interactions using models of transient storage. These studies are based on tracer-dilution data obtained during periods of steady flow. We present a modeling framework for the analysis of transient storage in stream systems with unsteady flows. The framework couples a kinematic wave routing model with a solute transport model that includes transient storage. The routing model provides time-varying flows and cross-sectional areas that are used as input to the solute transport model.

The modeling framework was used to quantify stream/substream interaction in Huey Creek, an Antarctic stream fed exclusively by glacial meltwater. Analysis of tracer-dilution data indicates that there was substantial interaction between the flowing surface water and the hyporheic (substream) zone. The ratio of storage zone area to stream cross-sectional area (A_s/A) was >1 in all stream reaches, indicating that the substream area contributing to hyporheic exchange was large relative to stream cross-sectional area. The rate of exchange, as governed by

the transient storage exchange coefficient (α), was rapid because of a high stream gradient and porous alluvial materials. Estimates of α generally exceed those determined for other small streams. The high degree of hyporheic exchange supports the hypothesis that weathering reactions within the hyporheos account for observed increases in solute concentration with stream length, as noted in other studies of Antarctic streams.

Key words: transient storage, hyporheic zone, McMurdo Dry Valleys, OTIS, tracer dilution, solute transport.

Recent studies of solute transport in streams have focused on the physical mechanisms affecting solute concentrations (Bencala et al. 1990, Stream Solute Workshop 1990, Castro and Hornberger 1991, Broshears et al. 1993, D'Angelo et al. 1993, Harvey et al. 1996, Morrice et al. 1997, Valett et al. 1997). These studies used tracer-dilution methods in which conservative tracers were added to the stream under study. Information from the tracer additions were then used in conjunction with transient storage models (e.g., Bencala and Walters 1983) to quantify stream hydrodynamics. Most studies to date have been conducted during periods of low flow, such that flow rates were nominally steady during the tracer addition. Small flow variations attributable to evapotranspiration may have occurred, but the effects on tracer concentrations were relatively small. Steady flow was therefore assumed, thereby simplifying the subsequent transport modeling.

Although the aforementioned studies are of great interest, many situations arise in which solute transport under unsteady flow conditions is important. Headwater systems, for example, are often subject to a "spring flush" wherein nutrients and trace metals are transported through the watershed during the rising limb of the hydrograph (e.g., Creed et al. 1996). In streams affected

by acid mine drainage and acid rain, large geochemical changes occur in response to rainfall and snowmelt events (e.g., episodic acidification, DeWalle and Swistock 1994). Desert streams are subject to frequent flash floods that alter hyporheic flow paths and stream geochemistry (Valett et al. 1990). Understanding of solute dynamics in these systems is clearly of importance. This understanding requires modeling techniques that rigorously consider the governing flow regime, thereby allowing the modeler to differentiate between physical/hydrologic and biogeochemical effects on solute concentration.

Kennedy et al. (1984) described an experiment wherein diel flow variations affected tracer concentrations. Jackman et al. (1984) applied a transient storage model to the resultant data set, using a simple hydrologic model and the assumption that stream cross-sectional area was temporally constant. This approach was adequate for the problem addressed by the authors, as the flow variations were relatively small. As flow variation increases, differences in wave celerity and mass transport become important, and more sophisticated techniques are needed. To this end, we present a method for the analysis of transient storage in streams that combines unsteady flow routing and solute transport. The technique presented is applied to Huey Creek, a glacial meltwater stream in the McMurdo Dry Valleys of Antarctica. The resulting work has implications for the design of tracer experiments in stream ecosystems as well as the study of solute transport in dilute Antarctic streams.

Methods

Site Description

The McMurdo Dry Valleys of Antarctica contain numerous glacial meltwater streams that drain into lakes on the valley floors (McKnight and Tate 1997). These glacial meltwater streams are complex hydrologic systems where flow rates vary in response to changes in temperature and light intensity (Conovitz et al. 1998). Rising lake levels in the dry valleys have been attributed to increased streamflow in these meltwater systems (Chinn 1993). As the main sources of water and nutrients, the streams are important when considering the potential effects of climate change on dry valley lakes (Doran et al. 1994).

Huey Creek is one of several streams draining into Lake Fryxell, a permanently ice-covered lake within a closed basin. As in most dry valley streams, streamflow in Huey Creek is derived from glacial meltwater, i.e., no appreciable inflow is added by surface or groundwater sources downstream from the glacier. Diel variations in air temperature and sun angle affect the generation of glacial meltwater, producing large flow variations during the day (Conovitz et al. 1998). Annual streamflow is also highly variable and dependent on the duration of temperatures $>0^{\circ}\text{C}$ and insolation during the austral summer (House et al., 1997).

Tracer experiment

Streams in the dry valleys are fed by cold-based glaciers that provide low ionic strength meltwater. Dry valley streams are therefore dilute systems; ionic strength generally increases with stream distance as waters interact with porous alluvial materials. These alluvial materials are

a source of minerals (e.g., calcite) and marine aerosols. The degree of interaction between the stream and the surrounding hyporheic (substream) zone is therefore of interest. This interaction may be investigated using the tracer-dilution method and transient storage modeling.

In January 1992, a tracer-dilution experiment was conducted in Huey Creek to determine the extent and rate of hyporheic exchange. A solution containing LiCl and LiBr was injected into Huey Creek beginning at 11:25 on 7 January. The injection continued at a rate of 8.7 mL/s for ~3.75 h. Injectate concentrations of Li and Br were 34 and 23 g/L, respectively. Water samples were collected at 8 downstream locations (Fig. 1). Samples were filtered and analyzed for Li (flame AA spectroscopy) and Br (ion-exchange chromatography). Chloride results are not reported here as the Cl added by the injection did not significantly influence ambient concentrations. Additional information on the tracer experiment is given by McKnight and Andrews (1993).

Lithium has been used as a conservative tracer in several acidic streams (e.g., Bencala et al. 1990). In circumneutral streams, Li may not be conservative because of the potential for cation exchange reactions on clay surfaces. These reactions are probably not significant in Huey Creek, however, as clays are not present and the streambed materials are relatively coarse. Lithium is therefore used as a conservative tracer throughout this study, an assumption that is examined in a later section.

Flow measurement

A Parshall flume provided a continuous streamflow record of Huey Creek above the outlet to Lake Fryxell (Fig. 1, site 945). Streamflow measurements from this site were fair to poor, with measurements errors potentially >15% (von Guerard et al. 1995). Flume estimates of streamflow varied from 50 to 120 L/s during the tracer addition. In addition to this continuous record, single

discharge measurements were obtained at sites 213, 457, and 610 (Fig. 1) using a pygmy meter and USGS stream gaging techniques. Additional information on the continuous streamflow record and single discharge measurements is provided by von Guerard et al. (1995).

Flow and transport modeling

Modeling framework.--Determination of a stream's transport characteristics provides a hydrologic setting from which to study biogeochemical processes. Temporal variation in streamflow may be neglected in many studies because the changes in flow are small over the relevant time scale. When flow variation is neglected, steady flow is assumed and tracer-dilution data is analyzed by direct application of a suitable transient storage model.

In our study, flow estimates from the Parshall flume indicated substantial diel variation in flow rate during the tracer addition. Given this large variation, the assumption of steady flow was not appropriate. The transient storage model used in this study was therefore linked to an unsteady flow routing model (Fig. 2). Within this modeling framework, temporal variations in volumetric flow rate (Q) and main channel cross-sectional area (A) were simulated using the flow routing model. These time-varying values were supplied as input to the transient storage solute transport model. Additional details on the flow and transport modeling components are provided below.

Unsteady flow routing.--The flow routing component of the modeling framework is based on the channel routing algorithms of DR₃M (Alley and Smith 1982), as implemented within the Modular Modeling System (Leavesley et al. 1996). The routing algorithms solve the 1-dimensional Saint-Venant equations for unsteady flow using the kinematic wave approximation. The governing equations conserve mass (continuity) and momentum. The continuity equation is given by:

$$\frac{\partial Q}{\partial x} + \frac{\partial A}{\partial t} = q_{LIN} \quad [1]$$

where A is the main channel cross-sectional area (m^2), Q is the volumetric flow rate (m^3/s), q_{LIN} is the lateral inflow rate (volumetric flow added by groundwater, interflow and overland flow, per unit stream length, $\text{m}^3/\text{s-m}$), t is time (s), and x is distance (m). Field observations of Huey Creek indicated that the channel was approximately rectangular. The kinematic wave approximation of the momentum equation for a rectangular channel is given by:

$$Q = \frac{S_o^{1/2} A^{5/3}}{w^{2/3} n} \quad [2]$$

where S_o is the bed slope, n is Manning's roughness coefficient, and w is channel width (m).

The first step in the routing procedure was to develop an inflow hydrograph at the upstream boundary (the injection point, site 0). Lithium tracer concentrations at the most upstream sampling location (site 9, Fig. 1) were used to estimate flow using the tracer-dilution method:

$$Q_0 = \frac{Q_i C_i}{(C_9 - C_b)} \quad [3]$$

where Q_0 is the flow at the upstream boundary (m^3/s), Q_i is the injection flow rate (m^3/s), C_i is the injectate concentration (mg/L), C_9 is the observed Li concentration at site 9 (mg/L), and C_b is the background Li concentration (mg/L). Observed Li concentrations (C_9) were compared to observed concentrations at site 213 to verify that sampled waters at site 9 were well mixed.

Equation 3 is applicable during the plateau period of the injection, i.e., after the tracer front arrives and C_9 is no longer changing because of mixing processes. As a result, the tracer-dilution method provided only a limited portion of the inflow hydrograph ($t = 11.75\text{-}14.83$ h). To provide the remaining portions of the inflow hydrograph, the continuous discharge record at site 945 was shifted backwards in time to represent the flow at site 0. The magnitude of the shift was

determined by comparing the rise of the hydrograph at site 945 with the rise in the hydrograph at the upstream boundary provided by tracer dilution (equation 3). The difference in the timing of the two hydrographs indicated a shift of 0.5 h.

Flow routing computations also required an approximation of channel geometry for the stream under study. Solution of equations 1 and 2 required estimates of bed slope, Manning's n , and channel width. Bed slope estimates were based on surveyed elevations available at ~30.5 m increments (E.D. Andrews, unpublished data). Values of Manning's n were obtained using Manning's equation and data from the single discharge measurements at sites 213, 457, and 610, i.e., Manning's n was back-calculated based on slope, flow velocity, and cross-sectional area.

Channel widths were available from the single discharge measurements at sites 213, 457, and 610 (1.0, 1.2, and 1.2 m, respectively). Average channel widths used in the routing model were adjusted upward from 0.4 to 0.6 m as part of the calibration process. Widths were adjusted such that simulated velocities agreed with velocities observed during the single discharge measurements (Table 1). This upward adjustment of stream width is consistent with the fact that discharge measurements were made at narrow, well-defined cross-sections. Estimates of Manning's n , bed slope, and channel width for the various flow routing reaches are summarized in Table 2.

The calibrated routing model provided a time series of flow and cross-sectional area at various downstream locations for use within the solute transport model. A comparison of routed flows and flows measured by the Parshall flume at site 945 shows that routed streamflow exceeded flume measurements during the peak of the hydrograph (Fig. 3). Because routed flow was based on tracer-dilution data, it included flow within the hyporheic zone. The lower flume discharges therefore suggests the existence of hyporheic flow paths that bypassed the flume.

Solute transport.--The rate and extent of hyporheic exchange may be quantified by applying a transient storage solute transport model to the tracer data. In this study we used OTIS (One-dimensional Transport with Inflow and Storage, Runkel 1998), a solute transport model that considers the physical processes of advection, dispersion, and transient storage. Model inputs include the time-varying flows and cross-sectional areas computed by the routing model and two parameters describing the process of transient storage (Fig. 2). These two parameters are the exchange coefficient, α (/s), and the cross-sectional area of the transient storage zone, A_s (m^2). In general, transient storage occurs because of solute detention in pockets of slow-moving water (i.e., side pools, eddies) and porous areas of the streambed (the hyporheic zone; Runkel and Bencala 1995). Huey Creek lacked side pools, so the transient storage parameters (α , A_s) are a direct measure of hyporheic exchange.

The governing equations describing the spatial and temporal variation in solute concentrations are given by:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}(AD\frac{\partial C}{\partial x}) + \frac{q_{LIN}}{A}(C_L - C) + \alpha(C_s - C) \quad [4]$$

$$\frac{dC_s}{dt} = \alpha\frac{A}{A_s}(C - C_s) \quad [5]$$

where C is the main channel solute concentration (mg/L), C_s is the storage zone solute concentration (mg/L), C_L is the lateral inflow solute concentration (mg/L), and D is the dispersion coefficient (m^2/s). All model parameters may vary on a reach-by-reach basis to reflect spatial variability. Numerical solution of equations 4 and 5 is described by Runkel and Chapra (1993, 1994).

Equations 4 and 5 describe the transport of conservative solutes. The solute transport model was therefore used to simulate the downstream transport of Li as a conservative tracer. Transient storage parameters for each stream reach were estimated by comparing the observed Li data with the model simulations. In many model applications, this parameter estimation process requires manual adjustment of the parameters to obtain close correspondence between simulated and observed tracer concentrations. This is a tedious trial-and-error procedure given the semi-empirical nature of α and A_s . The problem was further complicated in the present application, because flow rates were changing throughout the tracer-injection period. As an alternative to the trial-and-error approach, we obtained parameter estimates using nonlinear least squares (NLS; Wagner and Gorelick 1986, Runkel 1998). Final parameter estimates obtained by NLS are shown in Table 3.

Results and Discussion

Simulation results

Figure 4 (a-d) depicts simulated and observed Li concentrations at four downstream sampling locations. The simulations represent the best fit of the solute transport model to the Li data, as determined by NLS. Three distinct stages are evident in the observed concentration profiles. During the initial stage, Li concentrations rise dramatically as the tracer front arrives. This is followed by a >3-h period in which Li concentrations fluctuate in response to changes in streamflow. During the final stage, Li concentrations decrease slowly as the tracer front passes and tracer mass leaves the hyporheic zone. Simulated Li concentrations generally follow the observed data (Fig. 4a-d). Changes in streamflow simulated by the routing model allow the

transport model to follow the changes in concentration observed during the second stage. Failure to consider streamflow variability would result in a flat concentration profile (plateau) during this period.

The parameter values developed using the Li data may be used to predict the transport of other stream solutes, e.g., Br, another solute introduced by the tracer injection (Fig. 4e-h). Although observed Br concentrations are somewhat erratic, Br simulations based on the Li parameters indicate that the two solutes behaved similarly in Huey Creek. This result is in contrast to the findings of Bencala et al. (1990) for a metal-rich stream in which Br observations did not concur with Li-derived transport simulations.

The number of Br observations below the simulated concentration profile indicates that there may have been a slight loss of Br because of geochemical processes. The over-prediction of the Br profile also supports the assumption of conservative behavior for Li. If Br had been selected as the conservative tracer, simulations of Li based on Br-derived transport parameters would under-predict the Li profile. This under prediction would then suggest a source of Li in Huey Creek that was not identified during pre-injection sampling.

Huey Creek solute dynamics

Visual inspection of Huey Creek suggests that there was substantial interaction between the flowing surface water and the hyporheic zone. Flow was relatively shallow (0-30 cm) and the streambed was composed of coarse alluvial materials. The discrepancy between routed and measured streamflow shown in Fig. 3 also suggests hyporheic zone interaction. This interaction is confirmed by the tracer addition and transient storage modeling described above (Table 3). High values for the exchange coefficient, α , suggest a rapid exchange of water and solutes between the channel and the hyporheic zone. Exchange coefficient values for Huey Creek are substantially

higher than estimated values for several mountain streams (Fig. 5). The high rate of exchange in Huey Creek may be attributed to the high gradient of the stream (Table 2) and the porous nature of the alluvium.

Parameter values and 95% confidence intervals provided by the NLS procedure for transient storage area (Table 3) are plotted in Fig. 6. The relative size of the storage zone is frequently expressed as the dimensionless ratio, A_S/A . For unsteady flow, A_S/A in a given reach varies with A . Minimum and maximum values based on maximum and minimum stream cross-sectional areas are presented in Table 3. High values (>1) of A_S/A indicate that the substream area participating in hyporheic exchange was large relative to the stream cross-sectional area. Large values of A_S/A are also consistent with field observations. Parameter estimates for the first 3 reaches indicate that reach-to-reach variability in A_S was relatively low. An exception to this homogeneity is the large estimate of A_S in the final reach. This increase was due in part to the decrease in stream slope (Table 2); i.e., as the slope decreased, the stream spread out and had more interaction with the alluvium. Actual storage zone area for the final reach may have been considerably lower than the estimated value, however, given the 95% confidence interval shown in Fig. 6.

In summary, tracer-dilution data and transient storage modeling indicate that there was a high degree of hyporheic exchange within Huey Creek. Waters entering the hyporheic zone have a longer residence time than waters in the main channel. In addition, there is more intimate contact between the water and the surrounding substrate. These hydrologic factors promote weathering reactions such as the dissolution of calcite. The high degree of hyporheic exchange therefore supports the hypothesis of Green et al. (1989) that weathering reactions account for the

observed increase in solute concentration with stream length. Quantification of hyporheic processes should prove useful in studies of primary weathering in Antarctic systems (e.g., Lyons et al. 1997).

Steady flow comparison

To illustrate the importance of the unsteady flow modeling framework, the NLS procedure was used to determine parameter estimates and simulated Li concentrations for steady flow (Table 4). In this analysis, the volumetric flow rate (Q) and the stream cross-sectional area (A) were temporally fixed at 135 L/s and 0.16 m², respectively. These values were selected to represent average hydrologic conditions during the latter stages of the experiment ($t > 13$ h). The NLS procedure was therefore used to fit the recession of the tracer profile.

Parameter estimates for steady flow are given in Table 4. With the exception of reach one, there is an order of magnitude agreement between the estimated parameters and those obtained using the unsteady flow analysis (Table 3). Despite this general agreement, errors in the parameter estimates (relative to the unsteady flow estimates) were substantial (Table 4). These errors may potentially bias simulations of reactive transport (e.g., Runkel et al. 1996), thereby leading to incorrect analyses of stream geochemistry.

The assumption of steady flow resulted in an under-prediction of the Li concentration during the initial stages of the experiment (Fig. 7). In addition, simulated concentrations did not vary in response to changes in flow. These results are in contrast to the previous simulation that considers unsteady flow (Fig. 4b). This analysis shows that only a portion of the observed concentration profile may be simulated accurately under the assumption of steady flow.

Experimental design

The modeling work described above has several implications for the design of tracer-dilution/solute-transport experiments in streams. As shown in the present application, additional data collection activities should be undertaken when tracer-dilution methods are used during periods of unsteady flow. For this experiment, additional data collection included continuous measurement of discharge at site 945 and three single discharge measurements. As described previously, portions of the discharge record at 945 were used to create the inflow hydrograph at the upstream boundary of the system. Development of the inflow hydrograph based on downstream data (site 945) was required because a continuous record at the upstream boundary was unavailable. To avoid any errors associated with this approach, a more desirable set of data would include continuous discharge measurements at the upstream and downstream boundaries of the modeled system. Under this design, upstream discharge information could be combined with tracer-dilution data to create the inflow hydrograph. Data from the downstream discharge station could then be used to calibrate the flow routing model.

Another important aspect of the experimental design relates to the single discharge measurements taken at sites 213, 457, and 610. Measurements of velocity and stream cross-sectional area at these sites were combined with estimates of bed slope to determine Manning's n , a critical parameter in the flow routing procedure. An alternative approach is to determine n from tabulated summaries or empirical relationships. These relationships produce small values of n that when used within the routing model produce flow velocities in excess of observed values. Values of n determined via discharge measurements (0.054 - 0.10) are generally higher, suggesting greater roughness (and hence lower velocity). The increased roughness may be caused

by shallow flow depths (often <15 cm) and low water temperatures, two factors that may not be considered in the empirical relationships. The single discharge measurements are therefore an important part of the available data.

Model formulation

The solute transport model used for this work (OTIS, Runkel 1998) is based on the transient storage formulation presented by Bencala and Walters (1983). In this formulation, the exchange coefficient and transient storage area are treated as constants within a given reach. For unsteady flow applications, the formulation results in the assumption that α and A_S are unaffected by changes in flow, velocity, and stage. Several field observations suggest that this assumption is appropriate for Huey Creek. First, given the lack of side pools in Huey Creek, storage area is equivalent to the area of the hyporheic zone. Hyporheic zone area may be viewed as the product of the depth to permafrost and the width of the wetted streambed, two quantities that remained constant during the Huey Creek experiment. Second, the highly porous nature of the streambed suggests a large exchange coefficient that may be independent of the flow regime. The range of estimated values for α (Table 3, Fig. 5) also indicates that spatial variability may be more important than the temporal variability associated with changes in flow.

Our initial analysis of transient storage under unsteady flow relies on the model formulation described above. Future efforts could consider modifications to the model that express the transient storage parameters as functions of the flow regime. In regard to the exchange coefficient, several authors have noted an increase in the magnitude of α with increasing streamflow (D'Angelo et al. 1993, Harvey et al. 1996, Morrice et al. 1997). The physical reason for the increase in α with Q may be the corresponding increase in stream velocity (Q/A); i.e., higher stream velocities promote exchange between the active channel and the transient storage

zone. Empirical relationships between α and Q/A may therefore be developed. For A_S , the work of Harvey et al. (1996) and Morrice et al. (1997) indicates a decrease in both transient storage zone area and relative transient storage (A_S/A) with increasing streamflow. This decrease may be caused by the presence/absence of surface storage areas (i.e., pools and eddies) at low/high flow; i.e., pools at low flow may become active parts of the channel at high flow. Another possible explanation is an apparent insensitivity of the transient storage model to hyporheic exchange at higher flow (Harvey et al. 1996). These observations suggest empirical relationships between A_S (or alternatively A_S/A) and Q .

Another aspect of the model formulation described by Bencala and Walters (1983) is the assumption that water in the storage zone is immobile relative to water in the main channel. This assumption is based on work in mountain streams where there are zones of stagnant water and flow velocities through the hyporheic zone are low. In contrast, transient storage in Huey Creek appears to be dominated by flow through a porous hyporheic zone wherein flow velocities may be considerable. Alternate models that explicitly consider subsurface flow may therefore be of interest. Use of alternate models may be problematic, however, in that mechanistic descriptions of subsurface flow may introduce parameters that are difficult to identify using standard tracer techniques. This observation is in part responsible for the widespread use of the transient storage approach to date.

Solute transport under unsteady Flow

The modeling framework used to study Huey Creek combines a kinematic wave routing model with a transient storage solute transport model. Discussion of the numerical techniques underlying the transport model suggests that the model formulation may not be appropriate for the

analysis of solute transport under unsteady flow (Dawes and Short 1994, Runkel and Chapra 1994). The specific concern is that the numerical solution of equations 4 and 5 using a concentration boundary condition may not conserve mass given an unsteady flow regime. In order to test mass conservation, concentration-discharge profiles were integrated with respect to time to determine the mass passing a given sampling location. These integrated values agreed closely with the mass introduced via the upstream boundary condition; the maximum error at the five locations tested was 0.074% (Table 5). This low level of error indicates that mass is conserved and that the modeling approach used is appropriate for Huey Creek. In light of the large flow variation considered herein (Fig. 3), these results also suggest that the approach is appropriate for other unsteady flow applications.

Acknowledgements

The authors thank Sarah Spaulding and Mike Anthony for field and laboratory assistance. Ken Bencala provided valuable suggestions on the design of the tracer injection. Review comments were provided by Alex Blum and Jud Harvey. This work was supported by the US Geological Survey Water Resource Division and the NSF Office of Polar Programs (OPP 86-13607, OPP 88-17113 and OPP 92-11773).

Literature Cited

- Alley, W.M., and P.E. Smith. 1982. Distributed routing rainfall-runoff model, Version II, Computer program documentation, User's manual. US Geological Survey Open-File Report 82-344, NTSL Station, Mississippi.
- Bencala, K.E., D.M. McKnight, and G.W. Zellweger. 1990. Characterization of transport in an acidic and metal-rich mountain stream based on a lithium tracer injection and simulations of transient storage. *Water Resources Research* 26:989-1000.
- Bencala, K.E., and R.A. Walters. 1983. Simulation of solute transport in a mountain pool-and-riffle stream: a transient storage model. *Water Resources Research* 19:718-724.
- Broshears, R.E., K.E. Bencala, B.A. Kimball, and D.M. McKnight. 1993. Tracer-dilution experiments and solute-transport simulations for a mountain stream, Saint Kevin Gulch, Colorado. US Geological Survey Water-Resources Investigations Report 92-4081, Denver Colorado.
- Castro, N.M., and G.M. Hornberger. 1991. Surface-subsurface water interactions in an alluviated mountain stream channel. *Water Resources Research* 27:1991.
- Chinn, T.H. 1993. Physical hydrology of the dry valley lakes. Pages 1-51 *in* W.J. Green and E.I. Friedmann (editors). *Physical and biogeochemical processes in Antarctic lakes*. Antarctic Research Series, Volume 59, American Geophysical Union, Washington, DC.
- Conovitz, P.A., D.M. McKnight, L.M. MacDonald, A. Fountain, and H.R. House. 1998. Hydrologic processes influencing streamflow variation in Fryxell Basin, Antarctica. Pages 93-108 *in* J.C. Prisco (editor). *McMurdo Dry Valleys of Antarctica: a cold desert ecosystem*. Antarctic Research Series, Volume 72, American Geophysical Union, Washington, DC.
- Creed, I.F., L.E. Band, N.W. Foster, I.K. Morrison, J.A. Nicholson, R.S. Semkin, and D.S. Jeffries. 1996. Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. *Water Resources Research* 32:3337-3354.
- D'Angelo, D.J., J.R. Webster, S.V. Gregory, and J.L. Meyer. 1993. Transient storage in Appalachian and Cascade mountain streams as related to hydraulic characteristics. *Journal of the North American Benthological Society* 12:223-235.

- Dawes, W.R., and D. Short. 1994. Comment on “An efficient numerical solution of the transient storage equations for solute transport in small streams” by R.L. Runkel and S.C. Chapra. *Water Resources Research* 30:2859-2862.
- DeWalle, D.R., and B.R. Swistock. 1994. Causes of episodic acidification in five Pennsylvania streams on the northern Appalachian Plateau. *Water Resources Research* 30:1955-1963.
- Doran, P.T., R.A. Wharton, and W.B. Lyons. 1994. Paleolimnology of the McMurdo Dry Valleys, Antarctica. *Journal of Paleolimnology*. 10:85-114.
- Green, W.J., T.J. Gardner, T.G. Ferdelman, M.P. Angle, L.C. Varner, and P. Nixon. 1989. Geochemical processes in the Lake Fryxell Basin (Victoria Land, Antarctica). *Hydrobiologia* 172:129-148.
- Harvey, J.W., B.J. Wagner, and K.E. Bencala, 1996. Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange. *Water Resources Research* 32:2441-2451.
- House, H.R., D.M. McKnight, and P. von Guerard. 1997. The influence of stream channel characteristics on streamflow and annual water budgets for lakes in Taylor Valley. *US Antarctic Journal, Review* 1995, XXX:284-287.
- Jackman, A.P., R.A. Walters, and V.C. Kennedy. 1984. Transport and concentration controls for chloride, strontium, potassium and lead in Uvas Creek, a small cobble-bed stream in Santa Clara County, California, U.S.A., 2. Mathematical modeling. *Journal of Hydrology* 75:111-141.
- Kennedy, V.C., A.P. Jackman, S.M. Zand, G.W. Zellweger, and R.J. Avanzino. 1984. Transport and concentration controls for chloride, strontium, potassium and lead in Uvas Creek, a small cobble-bed stream in Santa Clara County, California, U.S.A., 1. Conceptual model. *Journal of Hydrology* 75:67-110.
- Leavesley, G.H., P.J. Restrepo, S.L. Markstrom, M. Dixon, and L.G. Stannard. 1996. Modular Modeling System (MMS): User’s manual. US Geological Survey Open-File Report 96-151, Denver, Colorado.

- Lyons, W.B., K.A. Welch, C.A. Nezat, D.M. McKnight, K. Crick, J.K. Toxey, and J.A. Mastrine. 1997. Chemical weathering rates and reactions in the Lake Fryxell Basin, Taylor Valley: comparison to temperate river basins. Pages 147-154 *in* W.B. Lyons, C. Howard-Williams, and I. Hawes (editors). Ecosystem processes in Antarctic ice free landscapes. Balkema Press, Rotterdam, The Netherlands.
- McKnight, D.M., and E.D. Andrews. 1993. Hydrologic and geochemical processes at the stream-lake interface in a permanently ice-covered lake in the McMurdo Dry Valleys, Antarctica. *Verh. Internat. Verein. Limnol.* 25:957-959.
- McKnight, D.M., and C.M. Tate. 1997. Canada Stream: a glacial meltwater stream in Taylor Valley, South Victoria Land, Antarctica. *Journal of the North American Benthological Society* 16:14-17.
- Morrice, J.A., H.M. Valett, C.N. Dahm, and M.E. Campana. 1997. Alluvial characteristics, groundwater-surface water exchange and hydrological retention in headwater streams. *Hydrological Processes* 11:253-267.
- Runkel, R.L., 1998, One dimensional transport with inflow and storage (OTIS): A solute transport model for streams and rivers. US Geological Survey Water-Resources Investigation Report 98-4018, Denver, Colorado.
- Runkel, R.L., and K.E. Bencala. 1995. Transport of reacting solutes in rivers and streams. Pages 137-164 *in* V.P. Singh (editor). Environmental hydrology. Kluwer, Dordrecht, The Netherlands.
- Runkel, R.L., and S.C. Chapra. 1993. An efficient numerical solution of the transient storage equations for solute transport in small streams. *Water Resources Research* 29:211-215.
- Runkel, R.L., and S.C. Chapra. 1994. Reply to comment on "An efficient numerical solution of the transient storage equations for solute transport in small streams" by W.R. Dawes and D. Short. *Water Resources Research* 30:2863-2865.
- Runkel, R.L., D.M. McKnight, K.E. Bencala, and S.C. Chapra. 1996. Reactive solute transport in streams 2. Simulation of a pH modification experiment. *Water Resources Research* 32:419-430.

- Stream Solute Workshop. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society* 9:95-119.
- Valett, H.M., C.N. Dahm, M.E. Campana, J.A. Morrice, M.A. Baker, and C.S. Fellows. 1997. Hydrologic influences on groundwater-surface water ecotones: heterogeneity in nutrient composition and retention. *Journal of the North American Benthological Society* 16:239-247.
- Valett, H.M., S.G. Fisher, and E.H. Stanley. 1990. Physical and chemical characteristics of the hyporheic zone of a Sonoran Desert stream. *Journal of the North American Benthological Society* 9:201-215.
- von Guerard, P., D.M. McKnight, R.A. Harnish, J.W. Gartner, and E.D. Andrews. 1995. Streamflow, water-temperature, and specific-conductance data for selected streams draining into Lake Fryxell, Lower Taylor Valley, Victoria Land, Antarctica, 1990-92. US Geological Survey Open-File Report 94-545, Denver, Colorado.
- Wagner, B.J., and S.M. Gorelick. 1986. A statistical methodology for estimating transport parameters -- theory and applications to one-dimensional advective-dispersive systems. *Water Resources Research* 22:303-315.

List of Figures

Figure 1: Map of Huey Creek showing tracer sampling and streamflow measurement stations. Site numbers refer to distance (m) from the tracer injection.

Figure 2: Modeling framework wherein output from flow routing model provides input to the transient storage solute transport model. A = main channel cross-sectional area. A_S = storage zone cross-sectional area. C = main channel solute concentration. n = Manning's roughness coefficient. Q = volumetric flow rate. Q_u = volumetric flow rate at upstream boundary. S_o = bed slope. t = time. w = stream width. α = exchange coefficient.

Figure 3: Comparison of routed streamflow and flume measurements at site 945.

Figure 4: Simulated and observed concentrations at downstream sampling locations (x). a-d.--Simulated Li profiles representing the best fit of the model to the Li tracer data. e-h.--Simulated Br profiles based on parameters from Li best fit.

Figure 5: Huey Creek exchange coefficients (α) compared with estimated exchange coefficients for other small streams (Broshears et al. 1993). Diamonds represent reach-specific parameter estimates.

Figure 6: Storage zone cross-sectional areas and 95% confidence intervals for each modeled stream reach.

Figure 7: Simulated and observed Li concentration at site 457. Simulated profile is based on the assumption of steady flow.

fig. 1

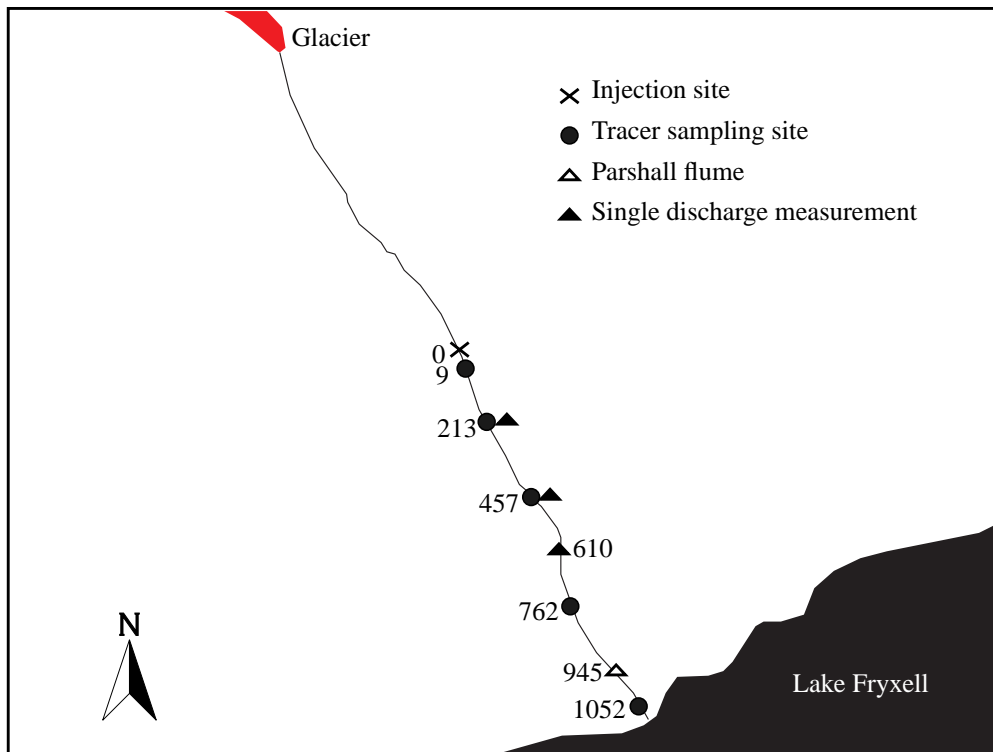


fig. 2

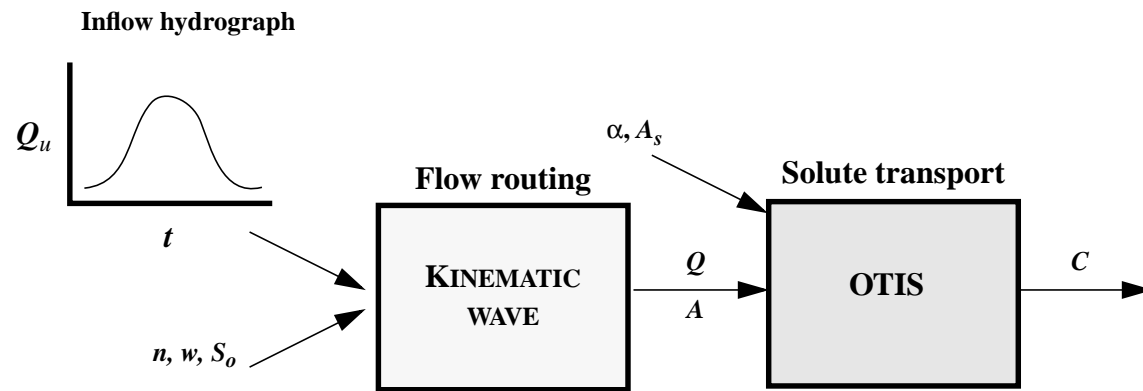


fig. 3

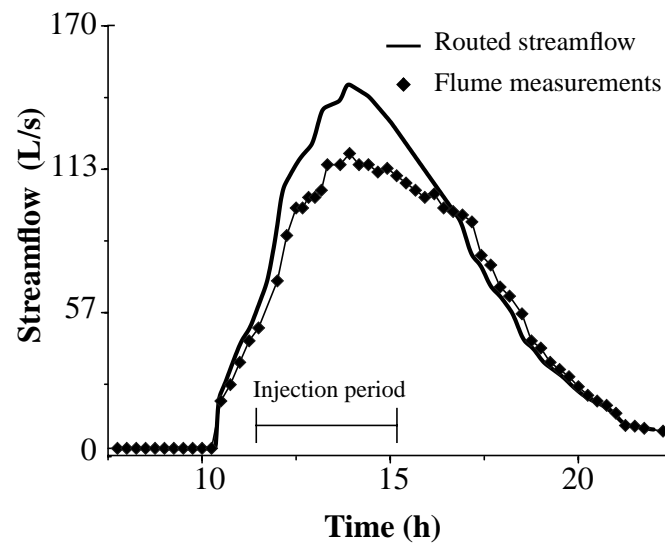


fig. 4

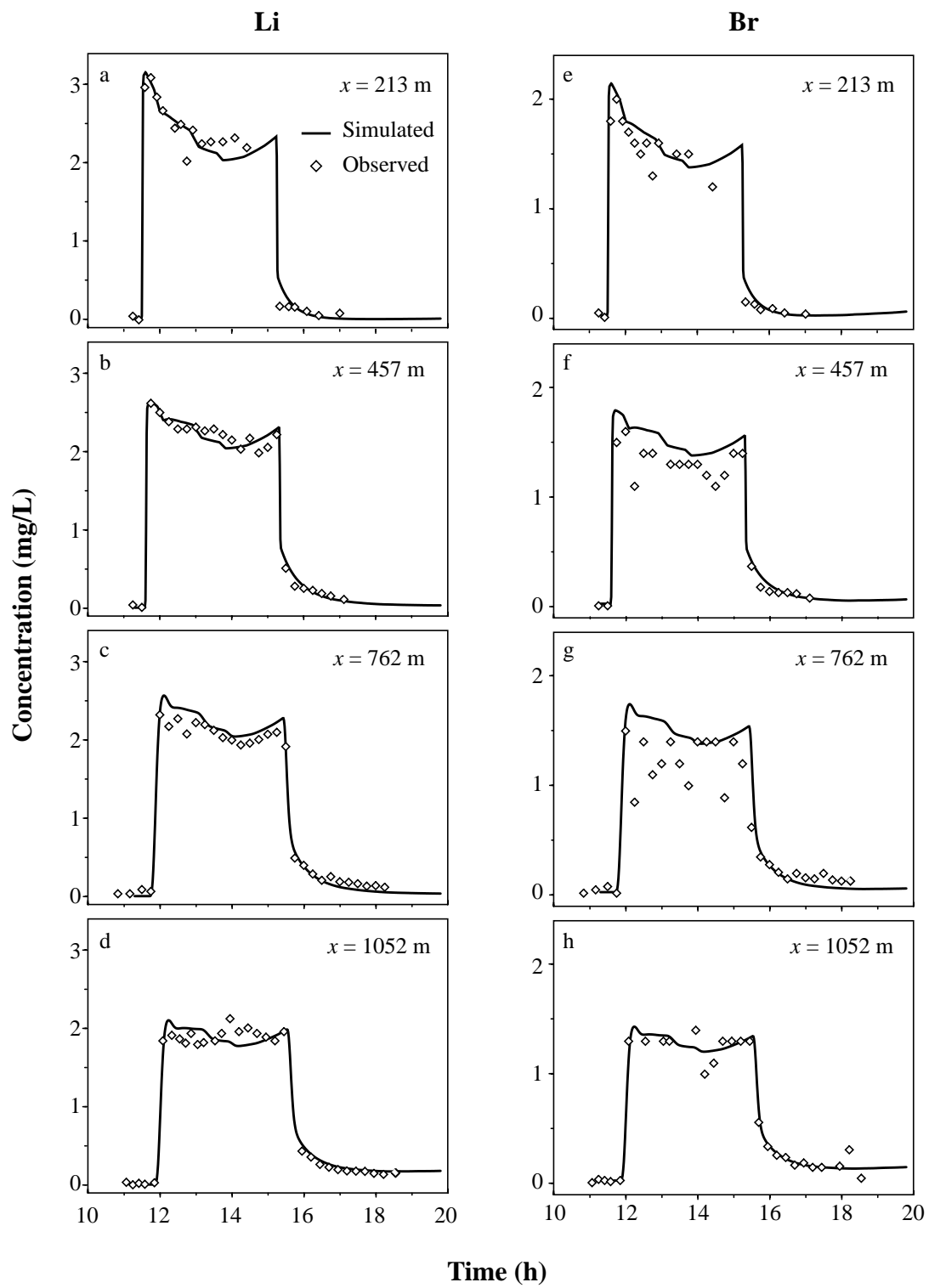


fig. 5

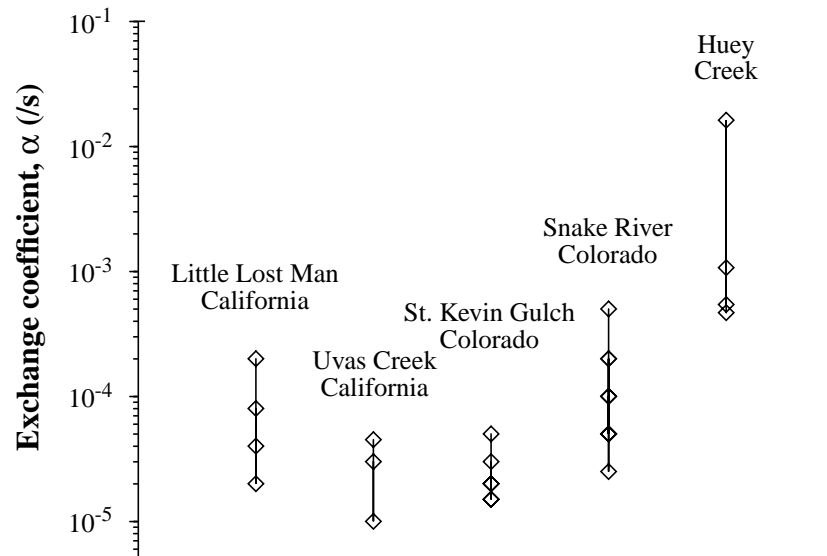


fig. 6

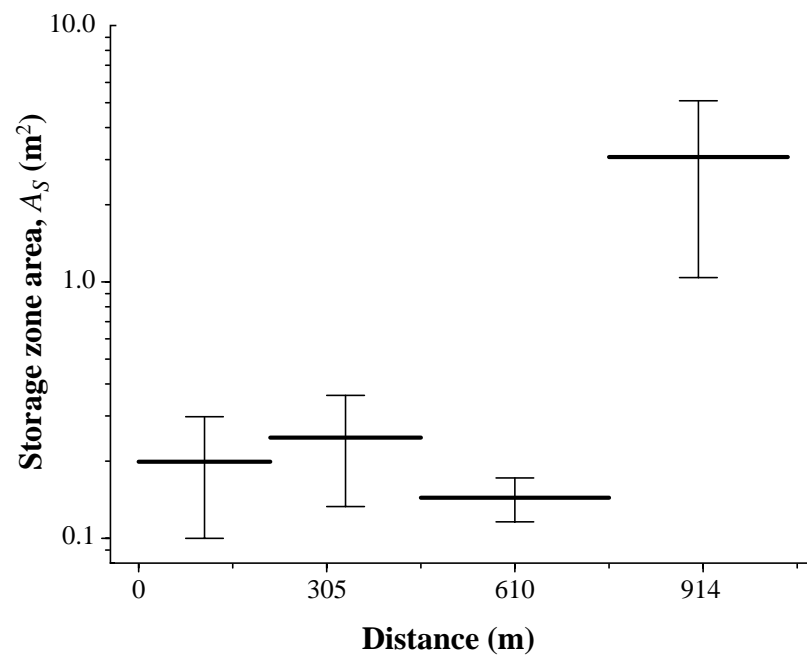


fig. 7

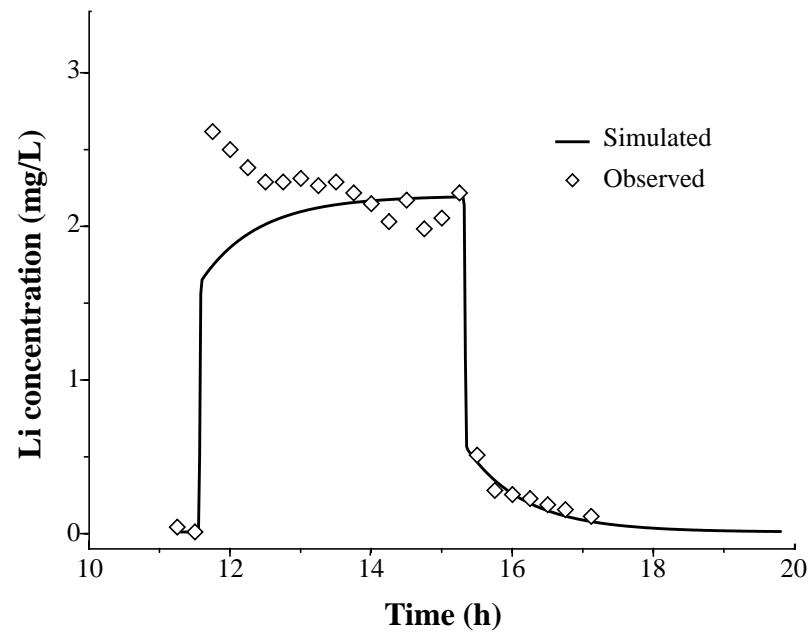


TABLE 1: Values from single discharge measurements (Obs. = observed) and flow routing computations (Sim. = simulated).

Gaging location (m)	Time (h)	Flow (L/s)		Area (m ²)		Velocity (cm/s)	
		Obs.	Sim.	Obs.	Sim.	Obs.	Sim.
213	11.8	93.4	90.6	0.13	0.13	73	73
457	12.3	101.9	113.3	0.12	0.14	85	85
610	12.7	96.3	121.8	0.12	0.15	79	79

TABLE 2: Parameter estimates used for flow routing computations.

Reach (m)	Bed slope, S_o (%)	Channel width, w (m)	Manning's roughness (n)
0-9	9.1	1.4	0.10
9-213	12.3	1.4	0.10
213-457	6.9	1.6	0.061
457-610	5.0	1.8	0.054
610-762	5.2	1.8	0.054
762-945	4.0	1.8	0.054
945-1006	1.9	1.8	0.054
1006-1052	1.1	1.8	0.054

TABLE 3: Transient storage parameter estimates under unsteady flow. A = main channel cross-sectional area. The dispersion coefficient (D) was set to 0.5 for all stream reaches

Reach (m)	Exchange coefficient, α (/s)	Storage zone area, A_s (m ²)	A_s/A	
			Min.	Max.
0-213	1.07×10^{-3}	0.20	1.1	1.8
213-457	5.43×10^{-4}	0.25	1.5	2.4
457-762	1.62×10^{-2}	0.14	0.8	1.4
762-1052	4.67×10^{-4}	3.07	15.9	34.3

TABLE 4: Transient storage parameter estimates under steady flow. Error = the relative error based on parameter estimate from unsteady flow analysis. The dispersion coefficient (D) was set to 0.5 for all stream reaches.

Reach (m)	Exchange coefficient, α (/s)		Storage zone area, A_s (m ²)	
	Estimate	% Error	Estimate	% Error
0-213	4.52×10^{-4}	-58	0.14	-30
213-457	6.42×10^{-4}	18	0.31	24
457-762	2.98×10^{-2}	84	0.26	86
762-1052	4.16×10^{-4}	-11	2.23	-37

TABLE 5: Mass balance errors at various reach end points.
Percent error was calculated by comparing simulated mass and total mass introduced by the upstream boundary condition (4003.94 mg).

Reach end point (m)	Simulated mass passing reach end point (mg)	% Error
9	4003.934	-0.00015
213	4005.333	0.035
457	4006.060	0.053
610	4005.430	0.037
762	4006.898	0.074